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(54) PROCESS FOR THE REMOVAL OF OXIDISABLE GASES FROM  
A GAS STREAM

(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organized and existing under the laws of the State of Delaware, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the removal of oxidizable gases, e.g. noxious gases, from a gas stream. More particularly, the invention relates to a process for the removal of such gases by washing the gas stream with an acidic aqueous solution containing oxidizing compounds.

Gas streams are often formed by the burning of various fuels in various industrial processes, e.g., in electric power generation, the smelting of ores, oil refining, and sulfuric acid and nitric acid manufacture. These streams, which are ultimately discharged into the atmosphere, often include gases which, when present in excessive concentrations are harmful to living organisms, in their environment.

In order to limit the amount of these oxidizable noxious gases entering the atmosphere and to comply with increasingly stringent governmental regulations, many processes have been proposed for removing them from gas streams. One such process involves the removal of SO<sub>2</sub> from flue gases by washing with sulfuric acid as taught in British Patent No. 930,584, German Patent Specification No. 1,234,912 and German Patent No. 670,966. These patents teach washing waste gases with an aqueous solution of between 35 and 80% by weight sulphuric acid containing persulfuric acid and hydrogen peroxide. The fraction of persulfuric acid consumed during the washing is regenerated by passing the used washing solution through an electrolytic cell and regenerating the persulfuric acid by anodic

oxidation. The persulfuric acid then partially equilibrates to form hydrogen peroxide. After regeneration, the washing solution is recycled.

Although it is asserted that the above process is economical because it depends solely upon a supply of electrical power and water, the process is not commercially feasible. The large investment in equipment necessary to form and maintain an electrolytic cell, the amount of factory space necessary to house the electrolytic cell and the number of man-hours necessary to operate the electrolytic cell on a satisfactory scale make the process commercially uneconomical.

Furthermore, since electrolytic regeneration of used washing solution is strongly inhibited by residual hydrogen peroxide and persulfuric acid concentration, it is necessary to program the washing cycle in such a manner as to minimize the amount of hydrogen peroxide and persulfuric acid present in the used solution during regeneration. Such a program can result in an unsatisfactorily low concentration of hydrogen peroxide and persulfuric acid in the washing solution, an uneconomically large absorbing tower in which the hydrogen peroxide and persulfuric acid are caused to react sufficiently or investment in additional equipment to remove the hydrogen peroxide and persulfuric acid sufficiently prior to regeneration. Thus the electrolytic process is not a commercially practical proposition.

In addition, in order to enhance the efficiency of electrolytic regeneration it is usually desirable to have halogen ions present in the liquid being electrolysed. Thus, it will typically be necessary to introduce halogen into the system, thereby introducing an impurity which must be subsequently removed and which itself is an environmental pollutant. This further reduces the desirability of a process dependent upon electrolytic regeneration.

Difficulties are also encountered with the electrolytic regeneration process in preventing noxious gas emission into the atmosphere above a given maximum level, e.g., in accordance with governmental regulations. For example, at plant start-up or as a result of normal fluctuations occurring during subsequent plant operation, the amount of persulfuric acid generated by electrolysis may not be enough to remove an excessive concentration of  $\text{SO}_2$  occurring in a waste gas stream.

Since gas streams containing oxidizable noxious gases are harmful to our ecology when discharged into the atmosphere and are coming under increasingly stringent governmental regulations, it would be desirable to have an economical process for adequately removing such gases from gas streams.

According to the present invention there is provided a process for the removal of an oxidizable gas from a gas stream which comprises washing the gas stream with an acidic aqueous solution containing an oxidizing compound comprising hydrogen peroxide or a reaction product thereof as herein defined in a washing zone, reactivating at least a portion of the solution by mixing it with preformed hydrogen peroxide and recycling the reactivated solution to the washing zone. The term "a reaction product of hydrogen peroxide" as used herein means any peroxyacid which is generated in the system by hydrogen peroxide.

The process according to the invention provides a method of removing oxidizable noxious gases from gas streams which is economical and commercially efficient. The amount of equipment, factory space, man-hours, and hydrogen peroxide required to successfully carry out the process on a satisfactory commercial scale is minimal.

The process according to the invention eliminates the necessity of programming the washing cycle in such a manner as to minimize the amount of oxidizing compounds present in the washing solution during reactivation since no substantial detrimental effect occurs from this presence. In fact, oxidizing compounds remaining in the used washing solution can be recirculated with the washing solution and will reduce the amount of preformed hydrogen peroxide required to be added to reactivate the use solution.

The process according to the invention also provides a method of controlling ultimate noxious gas emission into the atmosphere in accordance with governmental regulations. For example, during plant start-up or throughout plant operation, the amount of hydrogen peroxide contacting the gas stream can readily be increased as

the amount of noxious gas present in the gas stream increases.

As stated hereinbefore, the process according to the present invention relates to the removal of an oxidizable gas from a gas stream. The invention will hereinafter be described with particular reference to the removal of noxious gases from gas streams. The gas streams can be, for example, a stack gas from an electrical power generation station, a stack gas from various industrial heating units, a smelter off-gas, an oil refining off-gas, an off-gas from a sulfuric acid or nitric acid plant, a process gas in a sulfuric acid or nitric acid plant, an off-gas from a coke plant, or an off-gas from refuse-burning or other burning generations.

The amount of oxidizable noxious gas present in the gas stream can vary over a wide range. As the amount decreases, the amount of hydrogen peroxide necessary to give a satisfactory reduction of noxious gas in the stream decreases. The process is most economical when the amount of oxidizable noxious gas present in the gas stream is less than 5000 parts per million by volume and preferably less than 3500 parts per million by volume.

Although the process can be used to remove any oxidizable gas, it is most effective in the removal of oxidizable noxious gases selected from the group consisting of  $\text{SO}_2$ , NO, CO and  $\text{H}_2\text{S}$ . It is commercially advantageous to remove  $\text{SO}_2$  and NO since  $\text{SO}_2$  and NO are oxidised by active oxygen to compounds which with water form sulfuric acid and nitric acid, respectively, which are useful commercial acids. This process is thus particularly useful in removing  $\text{SO}_2$  and NO from waste gas streams in sulfuric acid and nitric acid plants respectively.

The removal of oxidizable noxious gas from the gas stream involves contacting the gas stream with an acidic aqueous solution of an oxidising compound comprising hydrogen peroxide or a reaction product of hydrogen peroxide as herein defined. The acidic aqueous solution enters a reaction zone or vessel, e.g., an absorbing or scrubbing tower as disclosed in British Patent No. 930,584. The scrubbing tower may contain any standard packing e.g., Intalox or Berl saddles, cross-partition, Raschig or Pall rings. The acidic aqueous solution contacts the gas stream which is proceeding through the reaction zone, preferably countercurrently, although co-current contacting is also feasible. The contact time is not critical but should be long enough to satisfactorily remove noxious gas, yet short enough to enable use of reasonably sized equipment. A preferred contact time is from 1 to 15 seconds and a most preferred time is from 2 to 8 seconds. The noxious gas is oxidized and removed from the gas stream, which

may then be released into the atmosphere or further processed.

The temperature at which the washing can be carried out can vary over a wide range, as will be appreciated by those skilled in the art. However, the temperature should be maintained below the boiling point of the acid used.

A preferred temperature range for removing  $\text{SO}_2$  from sulfuric acid plant off-gas is from 0 to  $100^\circ\text{C}$ .; the most preferred range is from  $40$  to  $80^\circ\text{C}$ . since this is the general temperature range of a sulfuric acid plant off-gas, and is thus a feature of particular convenience and efficiency of the process of the invention.

The used acidic aqueous solution, containing the reaction product of the oxidized noxious gas and having a reduced active oxygen content, is removed from the reaction zone and reactivated with preformed hydrogen peroxide. Reactivation is accomplished by mixing preformed hydrogen peroxide with the used acidic aqueous solution. The preformed hydrogen peroxide may be prepared by standard hydrogen peroxide production methods external to the process of the present invention and should be substantially free of persulfuric acid. The preformed hydrogen peroxide should be added in a stable form in order to facilitate the process and, accordingly, it is preferred to add the hydrogen peroxide as a preformed aqueous solution to the washing solution.

The amount of hydrogen peroxide added to reactivate the used washing solution depends upon the amount of oxidizable noxious gas present in the gas stream and the amount of such gas desired to be removed from the stream. It is preferred to add hydrogen peroxide to the used washing solution in an amount sufficient to reduce the amount of oxidizable noxious gas in the gas stream to less than 500 parts per million by volume, more preferably, to less than 300 parts per million by volume and most preferably to less than 100 parts per million by volume. Depending upon the amount of oxidizable noxious gas in the gas stream, the amount of hydrogen peroxide added to the washing solution can be varied, advantageously so as to maintain the weight percentage of oxidizing compounds in the washing solution in the washing zone at 0.01 to 25% by weight, preferably from 0.03 to 5% by weight and most preferably from 0.05 to 3% by weight.

After the reactivation with hydrogen peroxide, the acidic aqueous solution is returned to the reaction zone completing a cycle which can be continuously repeated. Washing solution volume and acid concentration can vary from wash to wash depending upon such factors as amount of water vapor in

the gas stream, amount of water added to the washing solution and amount of reaction product formed by oxidation of the noxious gases. The volume and acid concentration can readily be adjusted by adding water or acid to the solution or by removing a portion of the solution, preferably as a side-stream draw-off before peroxide reactivation. Adjustments can be made during each cycle, periodically after several cycles or, preferably, continuously as the washing solution is recycled.

The acid concentration can vary from 1 to 85% by weight, preferably from 5 to 75% by weight, and more preferably from 30 to 70% by weight. Solutions having acid concentrations less than about 1% are difficult to dispose of and solutions having concentrations greater than about 85% by weight acid are not sufficiently reactive.

A number of acids may be used to provide the acid aqueous solution. Suitable acids include, for example, sulfuric acid, nitric acid, hydrochloric acid, phosphoric acid, acetic acid, formic acid, carbonic acid, and mixtures of these.

When  $\text{SO}_2$  is present in the gas stream, it is preferred to employ a sulfuric acid washing solution. Thus, when the  $\text{SO}_2$  combines with hydrogen peroxide to form sulfuric acid, a portion of the washing solution approximating to the amount of sulfuric acid formed can readily be removed from the used washing solution and sold commercially. The process is facilitated by employing a sulfuric acid solution containing from about 30 to 70% by weight sulfuric acid as the washing solution.

It is similarly preferred to employ a nitric acid solution as the washing solution when  $\text{NO}$  is present in the gas stream since the nitric acid formed can readily be removed from the washing solution and sold commercially.

A preferred embodiment comprises passing a gas stream containing noxious gas through a reaction zone, continuously metering an acidic aqueous solution containing an oxidizing compound comprising hydrogen peroxide or a reaction product thereof as herein defined through the reaction zone, e.g., concurrently with or countercurrently to the gas stream, continuously removing a portion of the solution and optionally adding water to the remaining solution to maintain a desirable solution volume and acid concentration, reactivating the remaining solution with preformed hydrogen peroxide, and continuously metering the reactivated solution into the reaction zone.

An analyser, e.g., an automatic control mechanism, can be employed in the process to control hydrogen peroxide addition. The automatic control mechanism can analyse noxious gas content in the gas stream, e.g.,

either before or after washing, and affect, preferably simultaneously, the amount of hydrogen peroxide being mixed with the acidic aqueous washing solution by signaling a peroxide feed control unit. As the amount of noxious gas in the gas stream increases, the automatic control mechanism will signal the peroxide control unit to increase the amount of peroxide passing through to the acidic aqueous solution. However, as the amount of noxious gas decreases, the automatic control mechanism will signal the peroxide control unit to maintain or decrease the amount of peroxide passing to the acidic aqueous solution. A suitable analyser can be any standard analyser suitable for the purpose, e.g., a Photometric Analyser Model 400 or 460 sold by E.I. du Pont de Nemours and Company.

According to one preferred feature of the present invention, there is provided a process for the removal of an oxidizable noxious gas from a gas stream which comprises passing the gas stream through a washing zone, continuously metering an acidic aqueous solution containing an oxidizing compound comprising hydrogen peroxide or a reaction product thereof as herein defined into the washing zone, continuously removing a portion of the solution and optionally adding water to the remaining solution to maintain a desirable solution volume and acid concentration, reactivating the remaining solution by mixing at least a portion thereof with preformed hydrogen peroxide and continuously metering the reactivated solution to the washing zone.

According to a further preferred feature of the present invention, there is provided a process for the removal of sulfur dioxide from a gas stream at a temperature of from 40 to 80°C., which gas stream contains less than 3500 parts per million by volume of sulfur dioxide, which comprises countercurrently contacting the gas stream with an aqueous liquid at a temperature of from 40 to 80°C., which liquid contains from 30 to 70% by weight of sulfuric acid and from 0.03 to 3% by weight of hydrogen peroxide, and maintaining the oxidizing activity of the liquid by the addition of preformed hydrogen peroxide.

The following example will serve to illustrate the invention. All parts and percentages are by weight in the liquid phase and by volume in the gas phase unless otherwise indicated.

#### EXAMPLE

(A) A gas stream of 3300 ppm (parts per million)  $\text{SO}_2$  in air was passed through an 18" column having a 2" diameter backed with  $\frac{1}{4}$ " diameter glass rings at a rate of 138 lbs./hr. ft.<sup>2</sup>. Temperature in the column ranged from 50–60°C. An aqueous solu-

tion of 50% sulfuric acid and 0.41% oxidizing compounds, prepared by mixing an aqueous sulfuric acid solution with hydrogen peroxide, was passed through the column countercurrently to the gas stream at a rate of 848 lbs./hr. ft.<sup>2</sup>. The amount of  $\text{SO}_2$  remaining in the gas stream was reduced to 1400 ppm.

(B) The used washing solution of part (A) was adjusted to a concentration of 50% sulfuric acid and 0.42% oxidizing compounds by addition of sulfuric acid and hydrogen peroxide. A gas stream of 2625 ppm  $\text{SO}_2$  in air was passed through a column as in part (A) at a rate of 28.2 lbs./hr. ft.<sup>2</sup>. Temperature in the column ranged from 55–65°C. The adjusted solution was passed through the column countercurrently to the gas stream at a rate of 1970 lbs./hr. ft.<sup>2</sup>. The amount of  $\text{SO}_2$  remaining in the gas stream was reduced to 50 ppm.

(C) The used washing solution of part (B) was adjusted to a concentration of 50% sulfuric acid and 0.41% oxidizing compounds by addition of sulfuric acid and hydrogen peroxide. A gas stream of 3500 ppm  $\text{SO}_2$  in air was passed through a column as in part (A) at a rate of 35.5 lbs./hr. ft.<sup>2</sup>. Temperature in the column was 25°C. The adjusted solution was passed through the column countercurrently to the gas stream at a rate of 1970 lbs./hr. ft.<sup>2</sup>. The amount of  $\text{SO}_2$  remaining in the gas stream was reduced to 110 ppm.

(D) The used washing solution of part (C) was adjusted to a concentration of 50% sulfuric acid and 0.40% oxidizing compounds by addition of sulfuric acid and hydrogen peroxide. A gas stream of 3550 ppm  $\text{SO}_2$  in air was passed through a column as in part (A) at a rate of 86 lbs./hr. ft.<sup>2</sup>. Temperature in the column ranged from 60–65°C. The adjusted solution was passed through the column countercurrently to the gas stream at a rate of 1702 lbs./hr. ft.<sup>2</sup>. The amount of  $\text{SO}_2$  remaining in the gas stream was reduced to 680 ppm.

#### WHAT WE CLAIM IS:—

1. A process for the removal of an oxidizable gas from a gas stream which comprises washing the gas stream with an acidic aqueous solution containing an oxidising compound comprising hydrogen peroxide or a reaction product thereof as herein defined in a washing zone, reactivating at least a portion of the solution by mixing it with preformed hydrogen peroxide and recycling the reactivated solution to the washing zone.

2. A process as claimed in claim 1 wherein the oxidisable gas is a noxious gas.

3. A process as claimed in claim 2 wherein the gas is at least one gas selected from sulfur dioxide, nitric oxide, carbon monoxide and hydrogen sulfide.

4. A process as claimed in any of the preceding claims wherein the gas stream contains less than 5000 parts per million by volume of oxidizable gas.
5. A process as claimed in claim 4 wherein the gas stream contains less than 3500 parts per million by volume of oxidizable gas.
6. A process as claimed in any of the preceding claims wherein the gas stream is an SO<sub>2</sub>-bearing gas stream resulting from the manufacture of sulfuric acid.
7. A process as claimed in any of the preceding claims wherein the gas stream is subjected to washing for from 1 to 15 seconds.
8. A process as claimed in claim 7 wherein the gas stream is subjected to washing for from 2 to 8 seconds.
9. A process as claimed in any of the preceding claims wherein the acidic aqueous solution is reactivated by adding hydrogen peroxide in an amount sufficient to maintain a weight percentage of oxidizing compounds in the washing solution in the washing zone of from 0.01 to 25%.
10. A process as claimed in claim 9 wherein the said weight percentage is from 0.03 to 5%.
11. A process as claimed in claim 10 wherein the said weight percentage is from 0.05 to 3%.
12. A process as claimed in any of the preceding claims wherein the acidic aqueous solution contains at least one of sulfuric acid, nitric acid, hydrochloric acid, phosphoric acid, acetic acid, formic acid and carbonic acid.
13. A process as claimed in any of the preceding claims wherein the acidic aqueous solution has an acid concentration of from 1 to 85% by weight.
14. A process as claimed in claim 13 wherein the acid concentration is from 5 to 75% by weight.
15. A process as claimed in claim 14 wherein the acid concentration is from 30 to 70% by weight.
16. A process for the removal of an oxidizable noxious gas from a gas stream which comprises passing the gas stream through a washing zone, continuously metering an acidic aqueous solution containing an oxidizing compound comprising hydrogen peroxide or a reaction product thereof as herein defined into the washing zone, continuously removing a portion of the solution and optionally adding water to the remaining solution to maintain a desirable solution by mixing at least a portion thereof with preformed hydrogen peroxide and continuously metering the reactivated solution to the washing zone.
17. A process for the removal of sulfur dioxide from a gas stream at a temperature of from 40 to 80°C, which gas stream contains less than 3500 parts per million by volume of sulfur dioxide, which comprises countercurrently contacting the gas stream with an aqueous liquid at a temperature of from 40 to 80°C, which liquid contains from 30 to 70% by weight of sulfuric acid and from 0.03 to 3% by weight of hydrogen peroxide, and maintaining the oxidizing activity of the liquid by the addition of preformed hydrogen peroxide.
18. A process for the removal of an oxidizable gas from a gas stream substantially as herein described with reference to the Example.
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